Flue Gas Purification Utilizing SOx/NOx Reactions During Compression of CO_2 Derived from Oxyfuel Combustion (Oxy – T – Fired)

(NETL Cooperative Agreement No. DE-NT0005309)

Department of Energy/National Energy Technology Laboratory (DOE/NETL)
2010 CO2 Capture Technology R&D Meeting, 13-17 September 2010
Pittsburgh, PA, USA

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Air Products and Chemicals, Inc.

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Who Is Air Products?

- Global atmospheric, process and specialty gases, performance materials, equipment and services provider
  - Serving industrial, energy, technology and healthcare markets worldwide
- Fortune 500 company
- Known for our innovative culture and operational excellence
- Safety leader in the chemical industry
- Capture techniques
  - Based upon wide experience in ASU, HyCO, combustion applications, cryogenic separations, compression & CO_2 handling
  - Promising proprietary developments point to reductions in cost of CO_2 capture

Agreement Period of Performance & Cost Share

- **Period of Performance:**
  - **1 October 2008 – 30 September 2010**

Air Products	**$ 251,000 (20%)**
NETL Cost Share:	**$ 1,003,995 (80%)**
Overall Project Total:	**$ 1,254,995**

- **Project Participants: Air Products**
- **Host Site: Alstom Power - Power Plant Laboratories - Boiler Simulation Facility in Windsor, CT.**

Technology Fundamentals

- What is the technology?
- Current status of technology
- Design for the PDU (process development unit)
- Results from PDU campaigns
- Next Steps

Oxyfuel CO_2 Purification

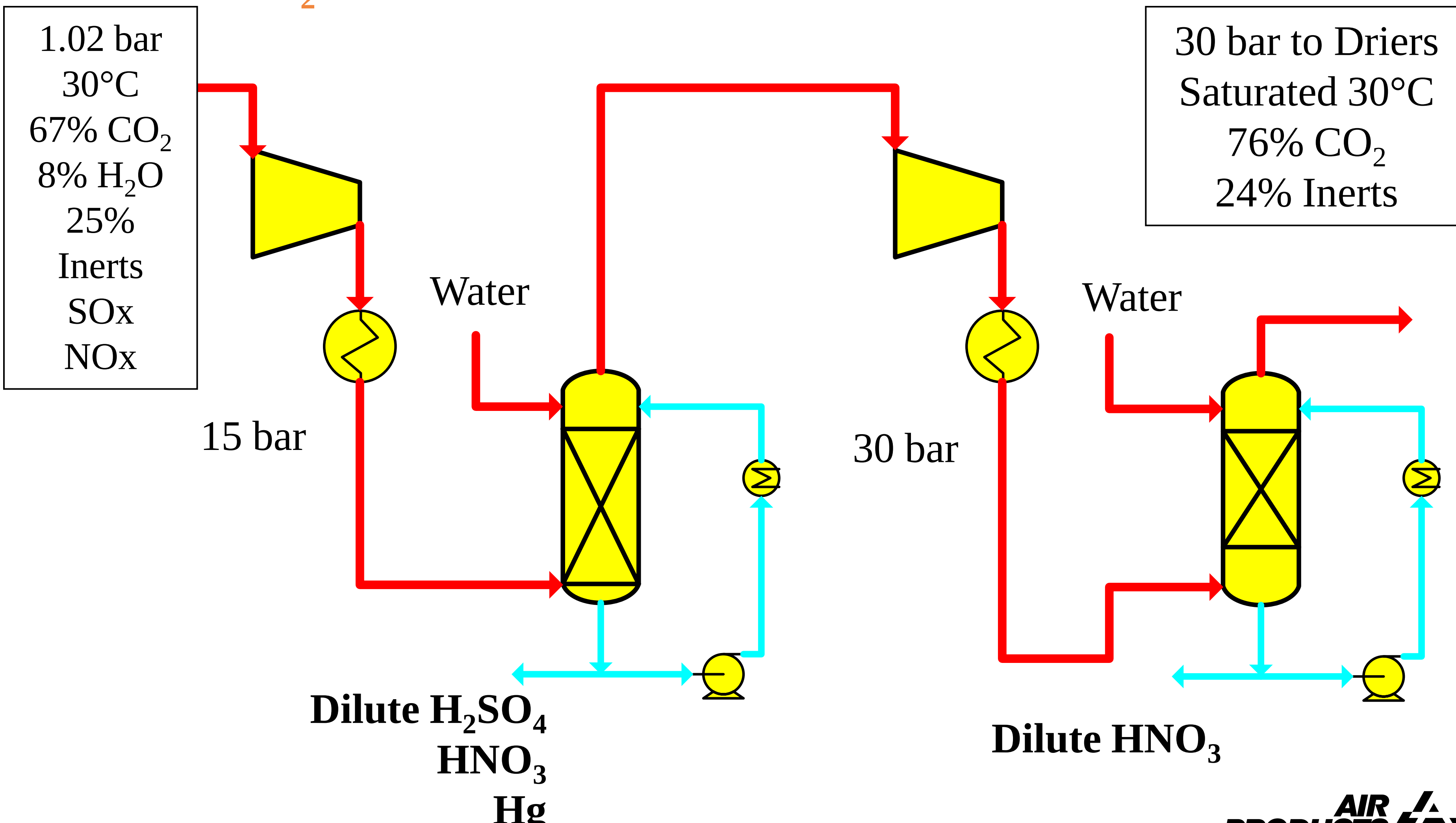
- **Oxyfuel combustion of coal produces a flue gas containing:**
  - **$CO_2 + H_2O$**
  - **Any inerts from air in leakage or oxygen impurities**
  - **Oxidation products and impurities from the fuel (SO_x, NO_x, HCl, Hg, etc.)**
- **Purification requires:**
  - **Cooling to remove water**
  - **Compression to 30 bar**
    - **Integrated SOx/NOx/Hg removal**
  - **Low Temperature Purification**
    - **Low purity, bulk inerts removal**
    - **High purity, Oxygen removal**
  - **Compression to pipeline pressure**

NOx SO_2 Reactions in the CO_2 Compression System

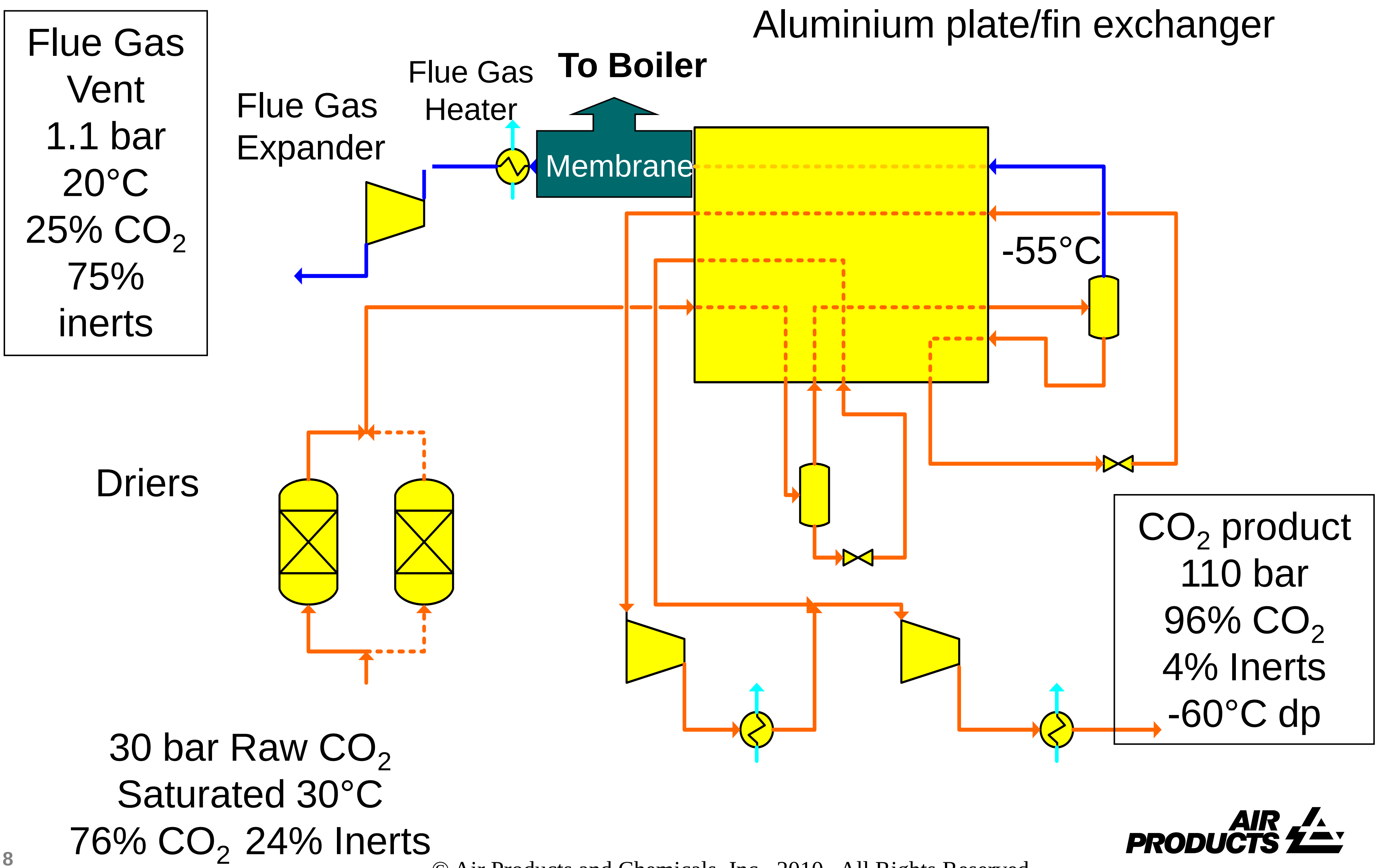
- **We realized that SO_2, NOx and Hg can be removed in the CO_2 compression process, in the presence of water and oxygen.**
- **SO_2 is converted to Sulfuric Acid, NO_2 converted to Nitric Acid:**
  - $NO + \frac{1}{2} O_2 = NO_2$ (1) Slow
  - $2\ NO_2 = N_2O_4$ (2) Fast
  - $2\ NO_2 + H_2O = HNO_2 + HNO_3$ (3) Slow
  - $3\ HNO_2 = HNO_3 + 2\ NO + H_2O$ (4) Fast
  - $NO_2 + SO_2 = NO + SO_3$ (5) Fast
  - $SO_3 + H_2O = H_2SO_4$ (6) Fast
- **Rate increases with Pressure to the 3rd power**
  - **only feasible at elevated pressure**
- **Little Nitric Acid is formed until all the SO_2 is converted**
- **Pressure, reactor design and residence times, are important.**

Air Products' CO_2 Compression and Purification System: Removal of SO_2, NOx and Hg

- SO_2 removal: 100%   NOx removal: 90-99%



Air Products' System: Inerts removal and compression to 110 bar



SOx/NOx Removal – Key Features

- Adiabatic compression to 15 bar:
  - No interstage water removal
  - All Water and SOx removed at one place
- NO acts as a catalyst
  - NO is oxidized to NO_2 and then NO_2 oxidizes SO_2 to SO_3: The Lead Chamber Process
- Hg will also be removed, reacting with the nitric acid that is formed
- FGD and DeNOx systems are not required for emissions or CO_2 purity
  - SOx/NOx removed in compression system
  - Low NOx burners are not required for oxyfuel combustion

Path to from Lab to Demo

Photo courtesy of Imperial College

Cylinder fed bench rig

Photo courtesy of Doosan Babcock

160 kW$_{th}$ oxy-coal rig

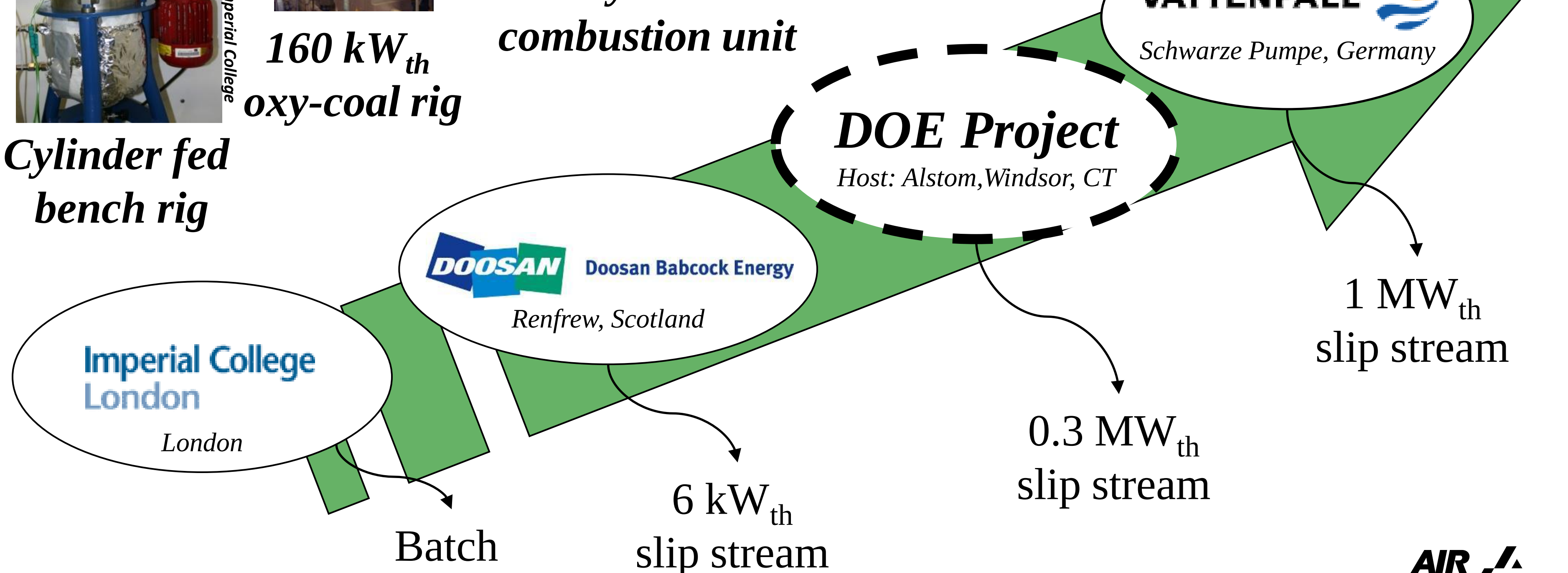
Photo courtesy of Alstom Power

15 MW$_{th}$ oxy-coal combustion unit

Photo courtesy of Vattenfall

30 MW$_{th}$ oxy-coal pilot plant

50-250 MW$_e$ oxy-coal Demonstration



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Project objectives

- **To purify the CO_2 derived from oxy-coal combustion by utilizing the SOx / NOx reactions that will occur during CO_2 compression**

Phase 1

Design and Construction of Reactor System for Purification of CO_2 from Oxy-Coal Combustion

- **The Phase I objectives include the design, construction, and commissioning of a 15 bar reactor system for removal of SOx /NOx from actual oxy-coal derived, CO_2-rich flue gas.**
- **The system will be designed to cool an oxy-coal combustion flue gas slip stream(~0.35 MW_{th} flow rate equivalent), compress from 1 bar to 15 bar and react within a 15 bar column the SOx/NOx present in the CO_2 rich flue gas.**

Project objectives (continued)

Phase II

Evaluate Robustness of Reactor Performance for Purification CO_2 from Oxy-Coal Combustion

- **The Phase II objectives include further evaluations of the reaction process using oxy-coal derived flue gas generated by the host site (Alstom).**
  - **Evaluate the performance of the reactor based on the reactor effluents for different reactor pressures as well as water recycle rates**
  - **Characterize the reactor effluents (both liquid and gaseous) to assess any change in reactor performance**
- **Air Products will develop an engineering model to describe the 15 bar purification reactor performance.**
  - **Perform a sensitivity analysis using said model to elucidate those parameters most critical to performance**

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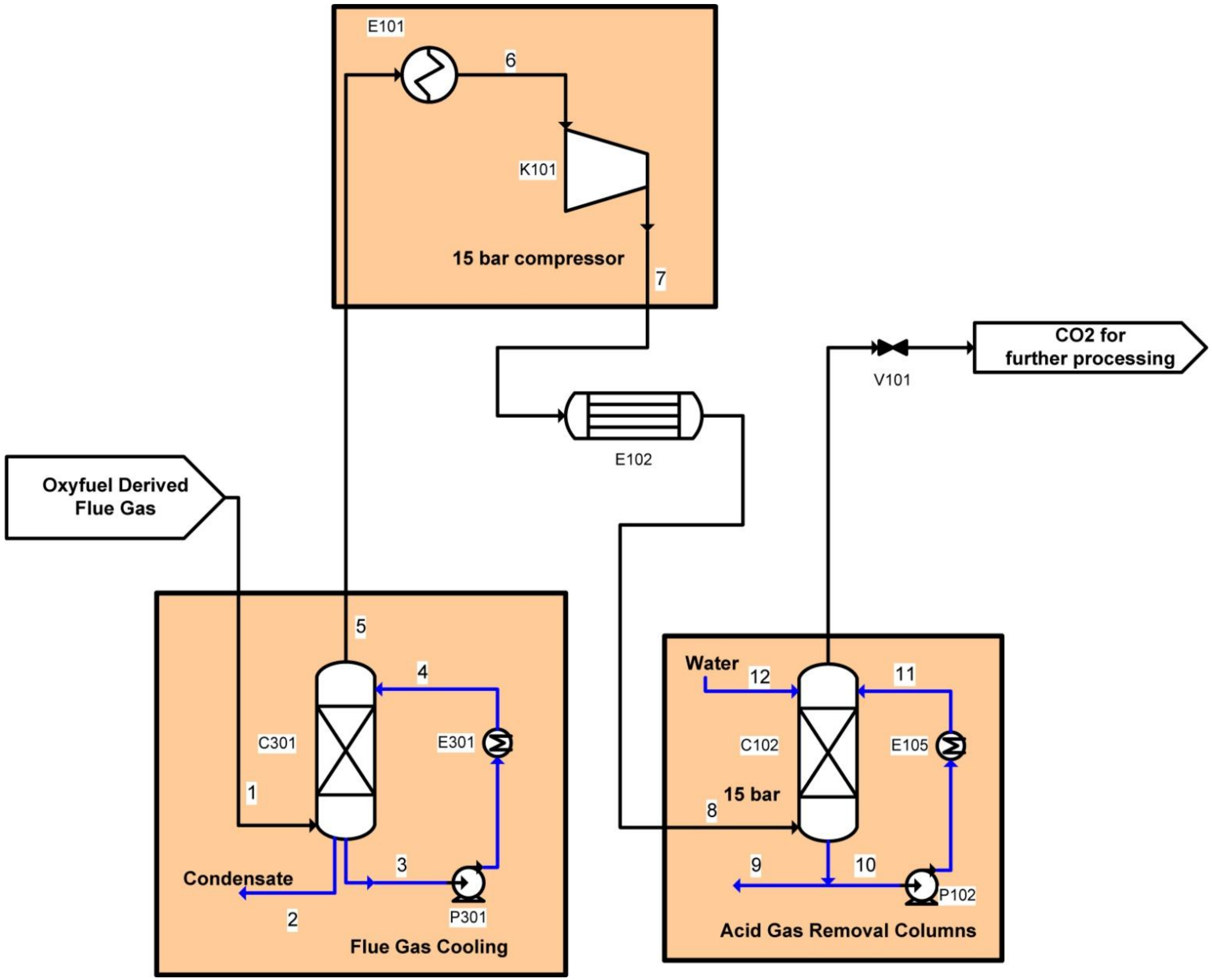
Milestones / Schedule

- Initiate Construction of Reactor System
  - Planned Date: Complete
- Initiate Testing of Reactor System
  - Planned Date: Complete
- Evaluate Performance of Reactor Based Flue Gas
  - Planned Date: Complete
- Develop Engineering Model and Perform Sensitivity Analysis
  - Planned Date: September 30, 2010

Current Process Flow Diagram



PDU (process development unit)

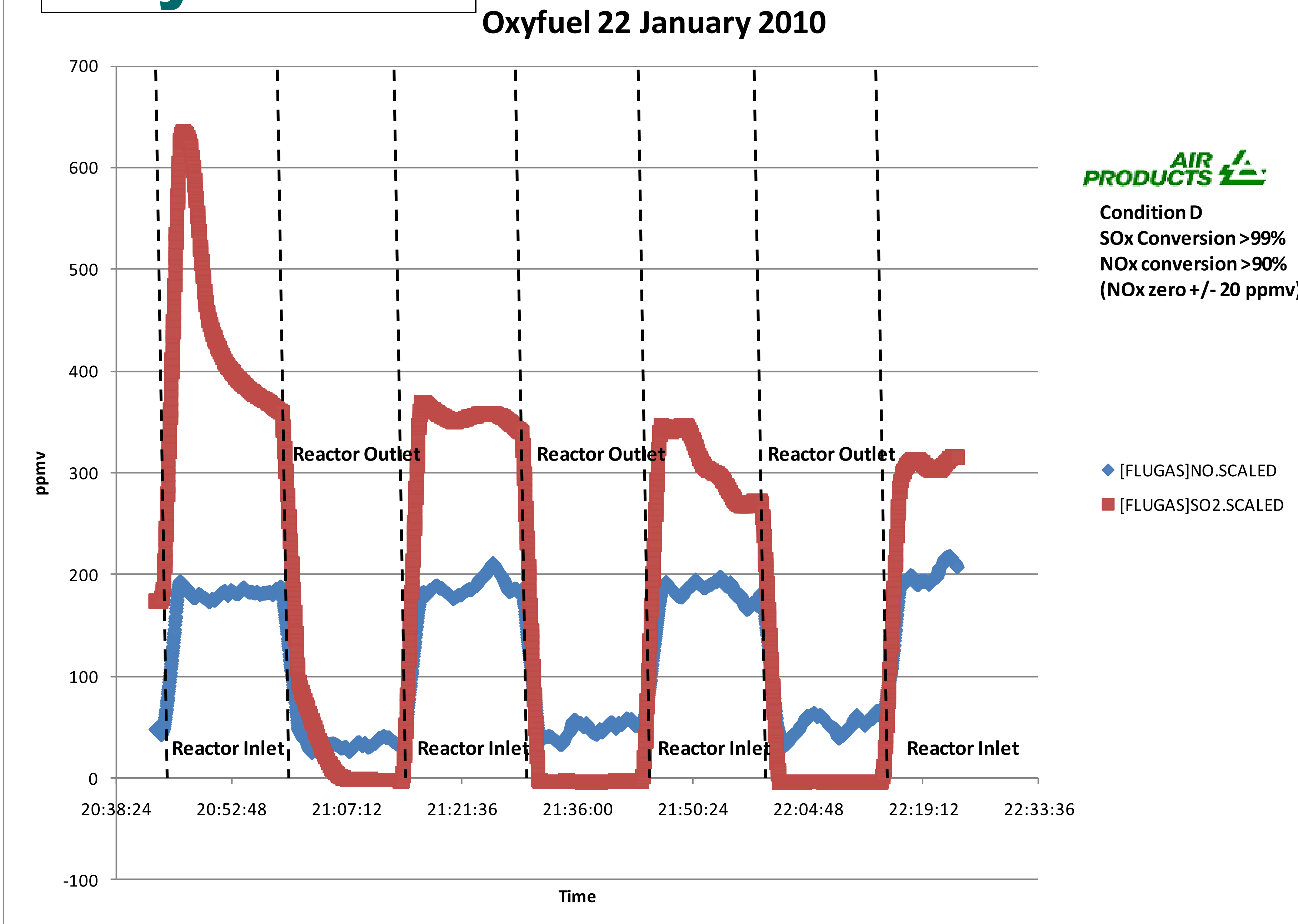
DOE Project: Air Products' Sour Compression PDU

Acid Reactor (C102)

Side View of PDU

- 1^{st} campaign Jan 2010
- 2^{nd} campaign April-May 2010

Key Results



Oxyfuel 22 January 2010
700
600
500
400
300
200
100
0
-100
ppmv
Reactor Outlet
Reactor Outlet
Reactor Outlet
Reactor Inlet
Reactor Inlet
Reactor Inlet
Reactor Inlet
20:38:24
20:52:48
21:07:12
21:21:36
21:36:00
21:50:24
22:04:48
22:19:12
22:33:36
Time
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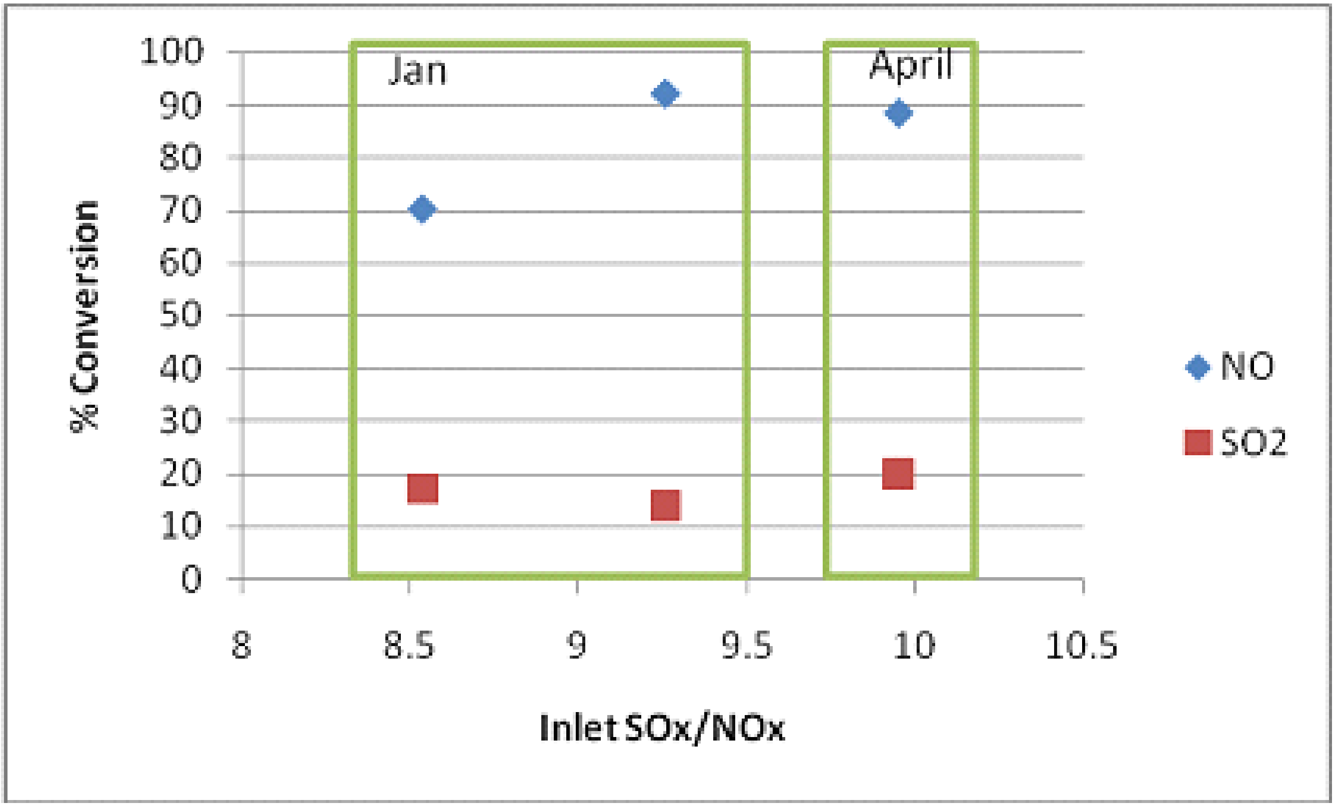
Condition D
SOx Conversion >99%
NOx conversion >90%
(NOx zero +/- 20 ppmv)
[FLUGAS]NO.SCALED
[FLUGAS]SO2.SCALED

Results

- **For the overall process, total SO_2 removal was 20-100 % (based on gas compositions).**
- **For the overall process, total NOx removal was 60-90 % (based on gas compositions).**
- **The effects of variations in the SO_2/NOx feed ratio, column pressure, gas flowrate and liquid recirculation on the reactor performance were elucidated. Process performance was most sensitive to SO_2/NOx feed ratio, over the range of parameter values investigated.**
- **SO_2 was removed from the flue gas through both sulfite and sulfate mechanisms.**

Comparison of NO and SO_2 conversions



- **Reproducing test conditions shows consistent results**
- **Confirms process and measurement reproducibility**

Impact of column operating parameters on SOx and NOx conversion

↑ in Operating Parameter	SO_x Conversion	NO_x Conversion
Column pressure	↑	↑
Column gas flow-rate	↓	↓
Column recirculation liquid flow-rate	↑	↑
Column fresh make-up water flow-rate	↑	↑
Column inlet SO_x/NO_x ratio	↓	↑

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Advantages

- FGD and DeNOx systems are not required for emissions or CO_2 purity
  - SOx/NOx removed in compression system
  - Low NOx burners are not required for oxyfuel combustion
- Oxygen can be removed to produce EOR-grade CO_2
- No penalty if CO_2 is required as a liquid
- Vent stream is clean, at pressure and rich in CO_2 (~25%) and O_2 (~20%)
  - Polymeric membrane unit – selective for CO_2 and O_2 – in vent stream will recycle CO_2 and O_2 rich permeate stream to boiler.
  - CO_2 Capture increase to >97%
  - ASU size/power reduced ~5%

Challenges

- Optimization of SOx, NOx, & Hg removal
- Reaction kinetics / equilibrium
- Fouling / impurities effects
- Materials of construction
- Byproduct streams – H_2SO_4, HNO_3, Hg species,…
- Burners must be demonstrated with flue gas recycle
- Minimization of parasitic power for O_2 supply and CO_2 compression / purification

- PDU
- CPU Pilot Plant

Boiler OEMs

Reference Plants Design
FEED Studies

Path to from Lab to Demo


Photo courtesy of Imperial College

Cylinder fed bench rig


Photo courtesy of Doosan Babcock

160 kW$_{th}$ oxy-coal rig


Photo courtesy of Alstom Power

15 MW$_{th}$ oxy-coal combustion unit


Photo courtesy of Vattenfall

30 MW$_{th}$ oxy-coal pilot plant

50-250 MW$_e$ oxy-coal Demonstration

Imperial College London
London

Batch

DOOSAN Doosan Babcock Energy
Renfrew, Scotland

6 kW$_{th}$ slip stream

DOE Project
Host: Alstom,Windsor, CT

0.3 MW$_{th}$ slip stream

VATTENFALL
Schwarze Pumpe, Germany

1 MW$_{th}$ slip stream

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Next Steps

- Complete final report for PDU / small scale testing of SOx/NOx removal
- Move to pilot scale for CO_2 purification and compression

- Scale up to Pilot: Underway
- Demonstration on stream: 2015
- Commercialization: 2017-2020

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Acknowledgment: **“This material is based upon work supported by the Department of Energy's National Energy Technology Laboratory under Award Number DE-NT0005309.”**

Thank you

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